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GASOLINE-WATER DISTRIBUTION COEFFICIENTS OF 27 AROMATIC AMINES

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Amine	Distribution coefficient on weight basis, K_{wt}	Distribution coefficient on volume basis[a], K_{vol}
Aniline	1.53	1.12
p-Toluidine	4.30	3.15
2-Methoxyaniline	5.15	3.77
o-Toluidine	6.24	4.58
m-Toluidine	6.37	4.66
2,6-Xylidine	16	12
Xylidines (technical)	20	15
2,4-Xylidine	20	15
2,5-Xylidine	22	16
N-Methylaniline	26	19
Pseudocumidine (technical)	28	21
Cumidines (from synthetic cumene)	51	37
N-Methyl-p-toluidine	54	40
p-Isopropylaniline	62	45
N-Isopropylaniline	62	45
N-Ethylaniline	69	51
2,4,6-Trimethylaniline	82	60
N-tert-Butylaniline	120	88
2-Methyl-5-isopropylaniline	130	95
p-tert-Butylaniline	140	105
N-Isopropyl-p-toluidine	150	110
2,4-Diethylaniline	210	155
N-Ethyl-p-toluidine	300	220
N-Propylaniline	330	240
N,N-Dimethylaniline	330	240
N-Butylaniline	600	440
N,N-Diethylaniline	3000	2000

[a]Calculated from distribution coefficient on weight basis.

The greater the distribution coefficient, the less will be the possible loss of additive when the fuel is stored over water. The aromatic amines are therefore listed in order of increasing suitability for overwater storage of their fuel blends.

INTRODUCTION

The present work, which is part of a general exploratory program on the use of aromatic amines as antiknock additives in aviation gasoline, concerns the suitability of 27 aromatic amines

for overwater storage of their gasoline blends. The general program also includes the determination of antiknock effectiveness, for which data have been reported for 19 amines (references 1 and 2) and the low-temperature solubility in gasoline, for which data have been reported for 15 amines (reference 3).

When gasoline containing an aromatic amine is stored in contact with water, as is the case in the widely used overwater storage systems, the water extracts a certain amount of the amine from the gasoline. The extent to which this removal of the amine can occur is governed by the distribution law. At equilibrium, the ratio between the concentrations of the amine in the two liquid phases of the gasoline-water system is constant at constant temperature. The ratio of the concentration of amine in the gasoline phase to that in the water phase at equilibrium is designated the gasoline-water distribution coefficient and is independent of the amount of fuel or water in the system. Briefly stated, the greater this distribution coefficient, the less will be the amount of amine leached out of the stored gasoline by the storage water. Relationships for estimating the concentration of amine in the residual gasoline as a function of the volume of gasoline stored in an overwater system have been derived, which utilize the distribution coefficient (reference 4.

The purpose of this report is to present experimentally determined gasoline-water distribution coefficients for 27 of the aromatic amines from the general program, to correlate molecular structure with distribution coefficient where possible, and to evaluate from these data the suitability for overwater storage of fuels containing the various amines.

Blends of 1, 3, and 6 percent by weight aromatic amines in an unleaded aviation gasoline containing 15 percent aromatics were tested. Previous data on xylidines (reference 5) have shown that temperature is the most significant variable affecting the distribution coefficient; consequently, the distribution coefficients were measured at 40° F and 100° F.

The general program was requested by the Army Air Forces, Materiel Command. The tests were performed at the NACA Aircraft Engine Research Laboratory, Cleveland, Ohio, between July 1943 and March 1944.

The data for all the aromatic amines in the program, whether for antiknock effectiveness, solubility at low temperatures, or overwater-storage suitability, are not as yet complete. When the

tests are concluded they, together with economic considerations, will indicate which aromatic amines are worthy of more extensive tests and more definite consideration as additives in aviation fuel.

BLEND CONSTITUENTS

The fuel used throughout the entire investigation was an unleaded grade 65 gasoline from which the aromatic hydrocarbons had been removed by successive extractions with 10 percent fuming sulfuric acid and silica gel (analysis showed less than 1 percent aromatics after extraction). A 15 percent by volume concentration of an aromatic-hydrocarbon mixture consisting of five parts xylene, two parts cumene, and one part toluene was then added. This fuel approximated the composition of typical current aviation fuels and also permitted specific knowledge of the aromatic content.

The aromatic amines tested, the physical constants of which are given in table I, either were purchased as the best grade obtainable and subsequently purified or were synthesized and purified at this laboratory. All are believed to be at least 95 percent pure. In several cases, namely where the literature on the compound and its properties was either missing or discrepant, purity of greater than 99 percent was attained for the compound in order to provide accurate physical constants to supplement the chemical literature.

APPARATUS AND PROCEDURE

Approximately 25-gram quantities of gasoline blends containing 1, 3, and 6 percent by weight of the amine were prepared, and a quantity of distilled water equal in weight to the gasoline was added. After tests with various types of bottles and closures, a 125-milliliter amber glass bottle provided with a screw cap fitted with a rubber gasket and a tinfoil liner was found to give satisfactorily reproducible results. This container was found to be leakproof and to eliminate variations in the analytical results caused by contamination or absorption of the sample by the bath water or by the closure material. The bottles and their contents were rotated on wheels in constant-temperature baths (40° F and 100° F) to attain equilibrium. Tests showed that equilibrium conditions were reached within 20 hours of agitation. After the agitation, specimens of the water layer were removed from the gasoline layer with a separatory funnel.

The water samples were analyzed with a commercial spectrophotometer having a quartz optical system and a 1-centimeter absorption cell. Ultraviolet light of approximately 2350 A wave length was

employed because of the distinctive light absorption exhibited by water solutions of aromatic amines at this wave length. The extinction of the sample, corrected by subtracting the extinction of a "blank" determination (that is, a water extract of amine-free gasoline) was compared with the extinction of standard water solutions of known amine concentrations. Extinction is the negative logarithm of the fraction of the incident light transmitted. For many of the amines it was necessary to dilute the samples quantitatively with distilled water to bring the observed absorption value within the range of the instrument.

Standard solutions were prepared either by dissolving a weighed amount of amine in water and diluting to the desired concentration or, where the surface tension of the amine prevented direct dissolution, by dissolving the amine with a measured quantity of acid, diluting, neutralizing the acid with a predetermined titer of base, and finally diluting to the desired concentration.

ACCURACY OF MEASUREMENTS

The uncertainties in the values of the distribution coefficients reported vary with the magnitude of the distribution coefficient. In general, the uncertainties will be smallest for the aromatic amines which have low distribution coefficients and greatest for the amines which have high distribution coefficients because the calculation of the distribution coefficient is dependent upon the accuracy of the spectrophotometric measurement of the aromatic-amine concentration in the water sample. This concentration can be determined with greatest accuracy when the amount of aromatic amine in the water is large; that is, when the magnitude of the correction for the blank determination is relatively small.

Errors in the measured concentrations of aromatic amines in water were caused by dilution of the water sample, spectrophotometric measurement of extinction, and correction for the blank sample. The average error is estimated to be about ±0.002 in each aromatic-amine concentration reported.

If the error in the amine concentration is assumed constant at ±0.002, the error in the distribution coefficient will be about ±0.3 when the distribution coefficient is 20 but, when the distribution coefficient is 200, the error will be about ±30, which is relatively about 10 times as large. If the practical aspects of the analyses are kept in mind, however, it is apparent that the need for accurate values of the distribution coefficients is greatest for the aromatic amine having low distribution coefficients, whereas, for distribution

coefficients greater than 200, the errors in the estimated losses
of an aromatic amine from a fuel blend stored over water are hardly
significant. (See reference 4.)

As a check on the accuracy of the spectrophotometric measure-
ments, water extractions were made of gasoline containing 1 percent
aniline at 40° F and 100° F and analyzed for aniline with the
spectrophotometer and by the Kjeldahl nitrogen method.. The results
were in good agreement, as indicated in the following table:

PERCENTAGE ANILINE IN WATER EXTRACTS OF

GASOLINE CONTAINING 1 PERCENT ANILINE

Temperature ($^\circ$F)	Spectrophotometer	Kjeldahl
40	0.405	0.401
100	.288	.291

CALCULATION OF DISTRIBUTION COEFFICIENTS

The distribution coefficients were calculated from the following
expression in which concentrations are expressed as percentages by
weight of each phase:

$$K_{wt} = \frac{W_r (W_w + W_e)}{W_e (W_g + W_r)} \tag{1}$$

where

$$W_e = \frac{W_w c_s}{100 - c_s} \tag{2}$$

$$W_r = W_o - W_e \tag{3}$$

Assuming the validity of the Beer-Lambert law,

$$c_s = \frac{E_s f - E_b}{k l} \tag{4}$$

and

$$k = \frac{E_{st}}{c_{st} \, l} \tag{5}$$

For these expressions

K_{wt} gasoline-water distribution coefficient (weight basis)

W_r weight of amine remaining in gasoline phase at equilibrium

W_e weight of amine extracted by water phase at equilibrium

W_w weight of water

W_g weight of gasoline

c_s concentration of amine in water sample, percentage by weight

W_o weight of amine originally in gasoline

E_s observed extinction of diluted water sample

E_b observed extinction of blank water sample obtained by shaking
distilled water with an equal weight of amine-free gasoline

E_{st} observed extinction of standard water solution

f sample dilution factor

k specific-extinction coefficient

c_{st} concentration of amine in standard water solution

l length of cell

Extinctions E_s, E_b, and E_{st} were corrected for differences in absorption-cell characteristics. The corrections were obtained by measuring the extinctions between the two cells when both were filled with distilled water.

Any distribution coefficient calculated on a weight basis may be converted to a volume basis by multiplying by the specific gravity of the gasoline solution:

$$K_{vol} = K_{wt}\left(\frac{\text{density of gasoline solution}}{\text{density of water solution}}\right) \qquad (6)$$

It should be noted that, although the distribution coefficient on a weight basis may be converted to a volume basis by this equation, the computed volume coefficient still pertains to the original weight

concentration of aromatic amine in the fuel blend. The volume concentration of aromatic amine in a fuel blend may be calculated from the weight concentration by the following formula:

$$c_{vol} = c_{wt} \frac{\rho_f}{\rho_a}$$

where

c_{vol} concentration of aromatic amine in fuel blend, volume basis

c_{wt} concentration of aromatic amine in fuel blend, weight basis

ρ_f density of fuel blend at temperature of measurement

ρ_a density of aromatic amine at temperature of measurement

RESULTS AND DISCUSSION

Table II presents the experimentally determined values of gasoline-water distribution coefficients arranged in order of increasing distribution coefficient for the aromatic amines tested.

Correlation of distribution coefficient with molecular structure. - In order to correlate readily distribution coefficient with molecular structure, distribution coefficients on a weight basis for solutions of 3 percent amine in gasoline at 40° F were plotted as figure 1. The following observations are apparent from this figure:

(a) The distribution coefficients showed approximately a 2000-fold range in value from aniline to diethylaniline.

(b) For a given aromatic nucleus, adding $-CH_3$ to N has a greater effect in increasing the distribution coefficient than adding $-CH_3$ to the ring or to a side chain.

(c) Increasing the chain length of an N-alkyl substituent increases the distribution coefficient for a given aromatic nucleus, which is evidenced by the solid lines through the N-alkylanilines and the N-alkyltoluidines.

(d) For a given aromatic nucleus, successively adding alkyl groups to N increases the distribution coefficient, demonstrated by the dotted lines through the N-alkyl and N,N-dialkylaniline.

(e) Increasing in any way the number of carbon atoms in the aryl radical increases the distribution coefficient. This increase is illustrated by numerous examples in the data, particularly by the broken (dot-dash) line through aniline, the toluidines, and the xylidines.

(f) For a given number of carbon atoms, branching of the alkyl chains attached to nitrogen decreases the distribution coefficient, as illustrated in the cases of N-propylaniline, N-isopropylaniline, N-butylaniline, and N-tert-butylaniline.

These observations would be the same for any of the other test conditions that may be selected.

Overwater storage of fuel blends. - In order to utilize these data successfully, it must be understood that the maximum extent to which water can extract an aromatic-amine additive from gasoline is essentially governed by the distribution law. Figure 2 presents the minimum possible additive concentration in the fuel remaining in the tank after part of the fuel is displaced from a full tank with amine-free water. Removal of the fuel in a single batch permits the greatest amine loss. Any stepwise removal of stored fuel will result in a lower loss of additive from the stored fuel than that indicated by figure 2. Figure 2 was derived from the equation of reference 4

$$X' = X\left(\frac{V_w + KV_{g'}}{V_{w'} + KV_{g'}}\right)$$

where

X' concentration of additive in gasoline after removal of batch of fuel

X concentration of additive in gasoline before removal of batch of fuel

V_w volume of water in tank before removal of batch of fuel

$V_{w'}$ volume of water in tank after removal of batch of fuel

$V_{g'}$ volume of fuel in tank after removal of batch of fuel

The greatest possible loss of additive from the gasoline remaining in the storage tank, however, seldom occurs in the use of the overwater fuel-storage systems. For example, analyses at intervals of the gasoline layer of tanks containing xylidine-blended fuel (reference 4) have shown that the loss of xylidine concentration from the fuel is

considerably less than that represented by figure 2. It seems likely
that, in practice, distribution of the aromatic amines between the
fuel and water layers is governed to a large extent by the rate of
diffusion of the amine through the solutions and across the liquid
interface, as well as by the equilibrium coefficient of distribution.

Obviously, the overwater storage of fuel blends of aniline,
which has a distribution coefficient of about 1.5, could result in
serious losses of the additive. Xylidines with a distribution coef-
ficient of about 20 have been stored over water without serious loss.

Losses of amines with distribution coefficients in the neighbor-
hood of 100 can be neglected except for the last portions of the fuel
withdrawn from the tank. Depletion of the additive from a small por-
tion of fuel may occur if extracted by a large volume of amine-free
water. This situation may be avoided, however, by not emptying the
tank of the last part of the amine-blended fuel.

SUMMARY OF RESULTS

Gasoline-water distribution coefficients were measured for
27 aromatic amines for 3 different concentrations at each of 2 tem-
peratures. The aromatic amines studied may be tabulated in order
of their decreasing suitability for overwater storage of their blends
as follows:

> N,N-Diethylaniline
> N-Butylaniline
> N,N-Dimethylaniline
> N-Propylaniline
> N-Ethyl-p-toluidine
> 2,4-Diethylaniline
> N-Isopropyl-p-toluidine
> p-tert-Butylaniline
> 2-Methyl-5-isopropylaniline
> N-tert-Butylaniline
> 2,4,5-Trimethylaniline
> N-Ethylaniline
> N-Isopropylaniline
> p-Isopropylaniline
> N-Methyl-p-toluidine
> Cumidines (from synthetic cumene)
> Pseudocumidine (technical)
> N-Methylaniline
> 2,5-Xylidine
> 2,4-Xylidine

Xylidines (technical)
2,6-Xylidine
m-Toluidine
o-Toluidine
2-Methoxyaniline
p-Toluidine
Aniline

Reference to figure 1 shows that the distribution coefficient can be increased by the following changes in molecular structure:

1. Addition of alkyl groups to either the N atom or to the aromatic nucleus

2. Substitution of straight carbon atom chains for branched chains of the same number of carbon atoms

3. Addition of a given alkyl group to N rather than to the aromatic nucleus

Aircraft Engine Research Laboratory,
    National Advisory Committee for Aeronautics,
        Cleveland, Ohio, August 3, 1944.

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TABLE I – PHYSICAL PROPERTIES OF AROMATIC AMINES TESTED

Amine	Boiling range at 760 mm ($^{\circ}$C)	Refractive index $n_{D}^{20^{\circ} C}$	Density at 20° C (grams/ml)
Aniline	184.0 – 184.5	1.5853	1.0220
N-Methylaniline	195.0 – 196.0	1.5704	.9860
N-Ethylaniline	203 – 204.0	1.5538	.9607
N-Propylaniline	220.5 – 223.5	1.5425	.9448
N-Isopropylaniline	206.5 – 209.0	1.5404	.9374
N-Butylaniline	240.0 – 240.5	1.5339	.9323
N-tert-Butylaniline	[a]95.0 (16 mm)	1.5270	.9244
N,N-Dimethylaniline	192.5 – 193.5	1.5580	.9564
N,N-Diethylaniline	215.0 – 217.0	1.5418	.9347
o-Toluidine	198.5 – 201.5	1.5718	.9989
m-Toluidine	202.5 – 203.5	1.5674	.9893
p-Toluidine	[b]44.0 – 44.4	————	
N-Methyl-p-toluidine	209.0 – 211.0	1.5570	.9610
N-Ethyl-p-toluidine	217.0 – 220.0	1.5439	.9441
N-Isopropyl-p-toluidine	222.0 – 223.0	1.5319	.9238
p-Isopropylaniline	225.5 – 226.5	1.5432	.9514
Cumidines(from synthetic cumene)	225.0 – 226.0	1.5448	.9536
p-tert-Butylaniline	[a]96.5 – 98.0 (5 – 6 mm)	1.5388	.9446
2,4-Xylidine	215.0 – 215.5	1.5591	.9751
2,5-Xylidine	216.0	1.5596	.9755
2,6-Xylidine	216.0 – 217.0	1.5616	.9768
2,4-Diethylaniline	241.0 – 242.0	1.5433	.9511
2-Methyl-5-isopropylaniline	240.0 – 242.0	1.5403	.9436
2,4,6-Trimethylaniline	[a]110.0 (15 mm)	1.5502	.9615
Pseudocumidine (technical)	225.0 – 241.0	1.5568	.9720
2-Methoxyaniline	224.0 – 225.0	1.5750	1.0931
Xylidines (technical)	216.0 – 219.5	1.5601	.9771

[a]Distilled under reduced pressure.

[b]Melting point instead of boiling range was measured for this solid.

National Advisory Committee
for Aeronautics

TABLE II – DISTRIBUTION COEFFICIENTS OF AROMATIC AMINES TESTED   13

Amine	Original concentration in fuel (percent by weight)	Temperature, °F					
		40			100		
		Concentration in water at equilibrium (percent by weight)	Distribution coefficient on weight basis K_{wt}	Distribution coefficient on volume basis[a,c] K_{vol}	Concentration in water at equilibrium (percent by weight)	Distribution coefficient on weight basis K_{wt}	Distribution coefficient on volume basis[b,c] K_{vol}
Aniline	1	0.405	1.48	1.08	0.287	2.50	1.76
	3	1.200	1.53	1.12	.850	2.57	1.81
	6	2.178	1.84	1.35	1.557	2.94	2.07
p-Toluidine	1	.196	4.12	3.02	.123	7.2	5.1
	3	.571	4.30	3.15	.352	7.6	5.4
	6	--------	--------	--------	.569	9.7	6.8
2-Methoxyaniline	1	.183	4.48	3.28	.129	6.8	4.8
	3	.491	5.15	3.77	.350	7.6	5.4
	6	.846	6.21	4.54	.632	8.6	6.1
o-Toluidine	1	.150	5.68	4.16	.096	9.4	6.6
	3	.415	6.24	4.58	.267	10.3	7.2
	6	.705	7.62	5.58	.480	11.6	8.2
m-Toluidine	1	.154	5.51	4.04	.104	8.6	5.7
	3	.410	6.37	4.66	.282	9.7	6.8
	6	.717	7.47	5.47	.505	11.0	7.7
2,6-Xylidine	1	.065	15	11	.040	24	17
	3	.173	16	12	.109	27	19
	6	.290	20	15	.190	31	22
Xylidines (technical)	1	.050	19	14	.033	29	20
	3	.143	20	15	.083	35	25
	6	.260	22	16	.157	37	26
2,4-Xylidine	1	.053	18	13	.031	31	22
	3	.142	20	15	.089	32	23
	6	.257	22	16	.170	34	24
2,5-Xylidine	1	.048	20	15	.029	33	23
	3	.132	22	16	.085	34	24
	6	.225	26	19	.149	39	27
N-Methylaniline	1	.041	23	17	.029	34	24
	3	.112	26	19	.076	39	27
	6	.195	30	22	.141	41	29
Pseudocumidine (technical)	1	.036	27	20	.022	45	32
	3	.103	28	21	.060	49	34
	6	.172	34	25	.108	55	39
Cumidines(from synthetic cumene)	1	.021	47	34	.013	76	54
	3	.059	51	37	.037	80	56
	6	.100	59	43	.066	90	63
N-Methyl-p-toluidine	1	.020	49	36	.013	76	54
	3	.055	54	40	.036	82	58
	6	.099	60	44	.066	90	63
p-Isopropylaniline	1	.021	47	34	.012	82	58
	3	.048	62	45	.033	90	63
	6	.077	77	56	.059	100	70
N-Isopropylaniline	1	.016	62	45	.012	82	58
	3	.048	62	45	.034	87	61
	6	.099	60	44	.064	93	65
N-Ethylaniline	1	.014	70	51	.009	110	78
	3	.043	69	51	.026	115	80
	6	.074	80	59	.050	120	85
2,4,6-Trimethylaniline	1	.013	76	56	.007	140	100
	3	.036	82	60	.021	140	100
	6	.065	91	67	.040	150	105
N-tert-Butylaniline	1	.010	100	73	.005	200	140
	3	.025	120	88	.014	210	150
	6	.043	140	105	.023	260	180
2-Methyl-5-isopropylaniline	1	.008	120	88	.005	200	140
	3	.023	130	95	.014	210	150
	6	.037	160	115	.026	230	160
p-tert-Butylaniline	1	.009	120	88	.005	200	140
	3	.021	140	105	.014	210	150
	6	.035	170	125	.027	220	155
N-Isopropyl-p-toluidine	1	.007	140	105	.005	200	140
	3	.020	150	110	.014	210	150
	6	.035	170	125	.022	270	190
2,4-Diethylaniline	1	.005	200	145	.003	300	210
	3	.014	210	155	.008	370	260
	6	.026	230	170	.014	430	300
N-Ethyl-p-toluidine	1	.004	250	180	.003	300	210
	3	.010	300	220	.008	370	260
	6	.017	350	260	.015	400	280
N-Propylaniline	1	.003	300	220	.002	500	350
	3	.009	330	240	.007	400	280
	6	.019	320	230	.013	460	320
N,N-Dimethylaniline	1	.003	300	220	.003	500	210
	3	.009	330	240	.008	370	260
	6	.017	350	260	.014	430	300
N-Butylaniline	1	.002	500	370	.001	1000	700
	3	.005	600	440	.004	800	550
	6	.009	700	500	.007	900	630
N,N-Diethylaniline	1	.0005	2000	1500	.0003	3000	2000
	3	.001	3000	2000	.0006	5000	4000
	6	.0015	4000	3000	.0008	8000	6000

[a]Density of gasoline solution at 40° F = 0.732 gram/ml.
[b]Density of gasoline solution at 100° F = 0.704 gram/ml.
[c]The values for K_{vol} were computed by multiplying the corresponding K_{wt} values by the density of the gasoline solution.

Figure I.— Gasoline-water distribution coefficients of aromatic amines. Solution, 3-percent amines in gasoline; fresh water; test temperature, 40°F.
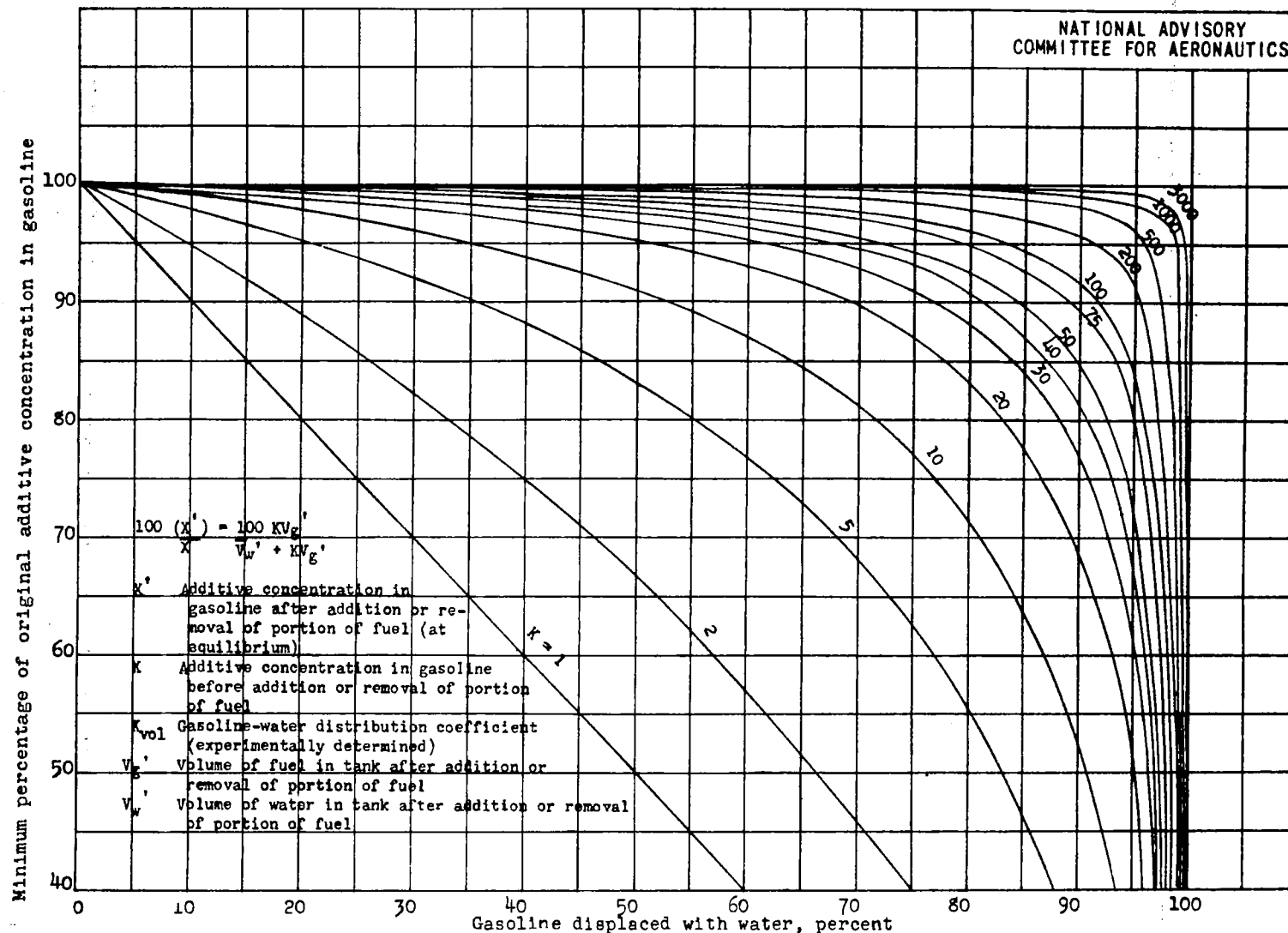
Figure 2. – Maximum possible loss of additive from fuel stored over water. A value for the distribution coefficient is required for the particular system, but the plot is independent of the original concentration of additive, nature of the two fluids, or temperature.